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(54) Title: AZEOTROPE-LIKE COMPOSITIONS OF DIFLUOROMETHANE, PENTAFLUOROETHANE AND 1,1,1-TRIFLUOROETHANE

(57) Abstract

The invention relates to azeotrope-like compositions of difluoromethane, pentafluoroethane and 1,1,1-trifluoroethane which are useful as refrigerants for heating and cooling applications and as blowing agents for the preparation of thermal plastic foam.

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AZEOTROPE-LIKE COMPOSITIONS OF DIFLUOROMETHANE, PENTAFLUOROETHANE AND 1,1,1-TRIFLUOROETHANE

Background of the Invention

Fluorocarbon based fluids have found widespread use in industry for refrigeration, air conditioning and heat pump applications.

Vapor compression is one form of refrigeration. In its simplest form, vapor compression involves changing the refrigerant from the liquid to the vapor phase through heat absorption at a low pressure and then from the vapor to the liquid phase through heat removal at an elevated pressure.

While the primary purpose of refrigeration is to remove energy at low temperature, the primary purpose of a heat pump is to add energy at higher temperature. Heat pumps are considered reverse cycle systems because for heating, the operation of the condenser is interchanged with that of the refrigeration evaporator.

Certain fluorocarbons, and in particular chlorofluorocarbons (CFC's), have gained widespread use in refrigeration applications including air conditioning and heat pump applications owing to their unique combination of chemical and physical properties. The majority of refrigerants utilized in vapor compression systems are either single component fluids or azeotropic mixtures. Single component fluids and azeotropic mixtures are characterized as constant-boiling because they exhibit isothermal and isobaric

evaporation and condensation. The use of azeotropic mixtures as refrigerants is known in the art. See, for example, R.C. Downing, "Fluorocarbon Refrigerants Handbook", pp. 139-158, Prentice-Hall, 1988, and U.S. Patents 2,101,993 and 2,641,579.

Azeotropic or azeotrope-like compositions are desired because they do not fractionate upon boiling or evaporation. This behavior is desirable because in the previously described vapor compression equipment with which these refrigerants are employed, condensed material is generated in preparation for cooling or for heating purposes, and unless the refrigerant composition is constant boiling, i.e., is azeotrope-like, fractionation and segregation will occur upon evaporation and condensation and undesirable refrigerant distribution may act to upset cooling or heating.

The art is continually seeking new fluorocarbon based azeotrope-like mixtures which offer alternatives for refrigeration and heat pump applications. Currently, fluorocarbons which contain little or no chlorine are of particular interest because they are considered to be environmentally acceptable substitutes for the fully halogenated CFC's which are suspected of causing environmental problems associated with the depletion of the earth's protective ozone layer. Mathematical models have substantiated that partially halogenated species, such as difluoromethane (HFC-32), penta-fluoroethane (125) and 1,1,1-trifluoroethane (HFC-143a), will not adversely affect atmospheric chemistry since they contribute negligibly to stratospheric ozone depletion in comparison to the fully halogenated species.

Substitute refrigerants must also possess those properties unique to the CFC's including chemical stability, low toxicity, and efficiency in-use. Efficiency in-use is important, for example, in refrigeration applications like air conditioning where a loss in refrigerant thermodynamic performance or energy efficiency may produce secondary environmental effects due to increased fossil fuel usage arising from an increased demand for electrical energy. Furthermore, the ideal CFC refrigerant substitute would not require major engineering changes to conventional vapor compression technology currently used with CFC refrigerants.

Description of the Invention

Our solution to the need in the art for stratospherically safer substitutes for CFC-based refrigerant compositions is mixtures comprising from about 90 to about 10 weight percent difluoromethane (HFC-32), from about 1 to about 75 weight percent pentafluoroethane (HFC-125) and from about 10 to about 40 weight percent 1,1,1-trifluoroethane (HFC-143a) which boil at about -53°C ± about 2°C at 760 mm Hg.

HFC-32 has been proposed as an environmentally acceptable refrigerant however, it is not a particularly efficient refrigerant especially at higher condensing temperatures, because it has a relatively low critical temperature. It is also flammable. HFC-143a is a good refrigerant on a thermodynamic basis but has a lower vapor pressure than HFC-32. This results in a lower refrigeration capacity than HFC-32. HFC-143a is also flammable. HFC-125 also has a lower capacity than HFC-32 but it is nonflammable. Applicants

have surprisingly discovered that when these compounds are combined in effective amounts, an azeotrope-like composition results which has a higher refrigeration capacity than HFC-32, HFC-143a and HFC-125 and which is nonflammable in certain proportions.

We have also discovered that the azeotrope-like compositions of the invention are useful as blowing agents for extruded thermal plastic foams such as polyethylene and polystyrene foams. When the compositions of the invention are used as blowing agents, they may be used alone or in combination with another liquid blowing agent such as 1,1-dichloro-1-fluoroethane (HCFC-141b) or other hydrochloro-fluorocarbon or hydrofluorocarbon liquids.

The compositions of the preferred and more preferred azeotrope-like compositions of the invention are summarized in Table I below. Note that the composition ranges reported are in weight percent and the term "about" is understood to preface each range disclosed.

Table I

Components	HFC-32	HFC-125	HFC-143a	Boiling Point at 760 mm Hg (°C)
Preferred Composition	85 - 10	1 - 60	15 - 30	about -53 ± about 2
More Preferred Composition	80 - 20	1 - 50	20 - 30	about -53 ± about 2
Another Preferred Composition	50 - 20	35 - 50	15 - 30	about -53 ± about 2

The precise or true azeotrope compositions have not been determined but have been ascertained to be within the indicated ranges. Regardless of where the true azeotrope lie, all compositions within the indicated ranges, as well as certain compositions outside the indicated ranges, are azeotrope-like, as defined more particularly below.

For purposes of this discussion, by azeotrope-like composition is intended to mean that the composition behaves like a true azeotrope in terms of its constant boiling characteristics or tendency not to fractionate upon boiling or evaporation. Thus, in such a system, the composition of the vapor formed during evaporation is identical or substantially identical to the original liquid composition. Hence, during boiling or

evaporation, the liquid composition, if it changes at all, changes only slightly. This is contrasted with non-azeotrope-like compositions in which the liquid and vapor compositions change substantially during evaporation or condensation.

In one process embodiment of the invention, the azeotrope-like compositions of the invention may be used in a method for producing refrigeration which comprises condensing a refrigerant comprising the azeotrope-like compositions and thereafter evaporating the refrigerant in the vicinity of the body to be cooled.

In another process embodiment of the invention, the azeotrope-like compositions of the invention may be used in a method for producing heating which comprises condensing a refrigerant in the vicinity of the body to be heated and thereafter evaporating the refrigerant.

In still another process embodiment of the invention, the azeotrope-like compositions of the invention may be used as a blowing agent in a process for making extruded thermal plastic foams comprising blending heat plasticized polyolefin resin with a blowing agent and introducing the resin/blowing agent blend into a zone of lower pressure to cause foaming. Generally, about 1 - 15 parts of blowing agent are utilized per 100 parts resin.

The difluoromethane, pentafluoroethane and 1,1,1-trifluoroethane components of the novel azeotrope-like compositions of the invention are known materials. Preferably they should be used in sufficiently high purity so as to avoid the introduction of adverse

influences upon the constant boiling properties of the system.

Example 1

This example confirms the existence of constant boiling or azeotrope-like compositions of HFC-32/HFC-125/HFC-143a via the method of distillation. It also illustrates that these mixtures do not fractionate during distillation.

A 150-plate packed distillation column with a liquid nitrogen condensed vapor dividing head was used for this example. The distillation column was charged with a 29/43.8/27.2 weight percent blend of HFC-32/HFC-125/HFC-143a respectively. The composition was heated under total reflux for about an hour to ensure equilibration. Vapor samples were taken from the top of the condenser and analyzed using gas chromatography. The averages of the vapor sample compositions and the overhead temperatures were quite constant within the uncertainty associated with determining the compositions, indicating that the mixtures are constant-boiling or azeotrope-like.

Example 2

The experiment outlined in Example 1 above is repeated for each of the following compositions:

a) 90-10/1-75/10-40 weight percent blend of HFC-32/HFC-125/HFC-143a respectively;

b) 10-85/1-60/15-30 weight percent blend of HFC-32/HFC-125/HFC-143a respectively;

c) 20-80/1-50/20-30 weight percent blend of HFC-32/HFC-125/HFC-143a respectively;

d) 20-50/35-50/15-30 weight percent blend of HFC-32/HFC-125/HFC-143a respectively.

The averages of the vapor sample compositions and the overhead temperatures are quite constant with the uncertainty associated with determining the composition, indicating that the compositions are constant-boiling or azeotrope-like.

Example 3

This example shows that azeotrope-like compositions of HFC-32, HFC-125 and HFC-143a have certain performance advantages when compared to HFC-32, HFC-125 and HFC-143a individually.

The theoretical performance of a refrigerant at specific operating conditions can be estimated from the thermodynamic properties of the refrigerant using standard refrigeration cycle analysis techniques. See, for example, "Fluorocarbons Refrigerants Handbook", ch. 3, Prentice-Hall, (1988) by R.C. Downing. The coefficient of performance, COP, is a universally accepted measure, especially useful in representing the relative thermodynamic efficiency of a refrigerant in a specific heating or cooling cycle involving evaporation or condensation of the refrigerant. In refrigeration engineering this term expresses the ratio of useful refrigeration to the energy applied by the compressor in compressing the vapor. The capacity of a refrigerant represents the volumetric efficiency of the

refrigerant. To a compressor engineer this value expresses the capability of a compressor to pump quantities of heat for a given volumetric flow rate of refrigerant. In other words, given a specific compressor, a refrigerant with a higher capacity will deliver more cooling or heating power.

We have performed this type of calculation for a medium to low temperature refrigeration cycle where the condenser temperature is typically 115°F and the evaporator temperature is typically -40°F. We have further assumed isentropic compression and a compressor inlet temperature of 65°F. Such calculations were performed for a 75/4/21 weight percent blend of HFC-32/HFC-125/HFC-143a respectively and for HFC-32 and HFC-125 alone.

Under the conditions specified above, the COP of the 75/4/21 weight percent HFC-32/HFC-125/HFC-143a blend was 1.66. The COP for each of HFC-32 and HFC-125 was 1.63 and 1.57 respectively. Thus, the energy efficiency of the mixture was higher than that of pure HFC-32 and HFC-125. Similarly, the capacity of the azeotropic blend was higher than that of HFC-32, HFC-125 and HFC-143a by 4%, 15% and 17% respectively.

Example 4

A small 304 grade stainless steel pressure vessel is constructed using schedule 40 pipe which is 4 inches in length and 2 inches in diameter. The vessel has top and bottom flanges which are used to close the ends of the cell. A pressure tight seal is maintained between the ends of the pipe and the flanges using Teflon o-rings. The vessel is closed by tightening 4

bolts which run the length of the cell through the top and bottom flanges. The design pressure limit for the apparatus is 1700 psi at 200°C; the operational limit is set at 1000 psi.

Three grams of very finely ground Dow Styrene 685D is placed into a 3 inch x 1.5 inch open glass jar. The glass jar is then placed in the pressure vessel and the pressure vessel is closed and evacuated.

Twenty two and one half grams of the composition of Example 1 is charged into the sealed vessel. The vessel is placed in a 250°F oven overnight. The vessel is removed from the oven, rapidly depressurized and then immersed in water. The glass jar is removed from the vessel. The resulting foam has a density of 3 - 4 lbs/ft^3 indicating that the composition of Example 1 is a good blowing agent for thermal plastic foam.

In summary, we have discovered that compositions of HFC-32, HFC-125 and HFC-143a are azeotrope-like, useful as blowing agents for thermal plastic foam and polyurethane foam and exhibit improved refrigeration properties.

Example 5

The experiment outlined in Example 4 above is repeated using each of compositions a)- d) of Example 2. In each case, the resulting foam has a density of 3 - 4 lbs/ft^3 indicating that each of compositions a) - d) is a good blowing agent for thermal plastic foam.

What is Claimed:

1. Azeotrope-like compositions consisting essentially of from about 90 to about 10 weight percent difluoromethane, from about 1 to about 75 weight percent pentafluoroethane and from about 10 to about 40 weight percent 1,1,1-trifluoroethane which boil at about -53°C at 760 mm Hg.

2. The azeotrope-like compositions of claim 1 wherein said compositions boil at -53°C ± about 2°C at 760 mm Hg.

3. The azeotrope-like compositions of claim 1 consisting essentially of from about 85 to about 10 weight percent difluoromethane, from about 1 to about 60 weight percent pentafluoroethane and from about 15 to about 30 weight percent 1,1,1-trifluoroethane.

4. The azeotrope-like compositions of claim 1 consisting essentially of from about 80 to about 20 weight percent difluoromethane, from about 1 to about 50 weight percent pentafluoroethane and from about 20 to about 30 weight percent 1,1,1-trifluoroethane.

5. The azeotrope-like compositions of claim 1 consisting essentially of from about 50 to about 20 weight percent difluoromethane, from about 35 to about 50 weight percent pentafluoroethane and from about 15 to about 30 weight percent 1,1,1-trifluoroethane.

6. A method for producing refrigeration which comprises condensing a composition of claim 1 and thereafter evaporating said composition in the vicinity of a body to be cooled.

7. A method for producing heating which comprises condensing a composition of claim 1 in the vicinity of a body to be heated and thereafter evaporating said composition.

8. A process for making extruded thermal plastic foams comprising blending heat plasticized polyolefin resin with a composition of claim 1 and introducing the blend into a zone of lower pressure to cause foaming.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 C09K5/04 C09K3/30 C11D7/50

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 5 C09K C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DATABASE WPI Section Ch, Week 9136, Derwent Publications Ltd., London, GB; Class E16, AN 91-262358 & JP,A,3 170 588 (MATSUSHITA ELEC IND KK) 24 July 1991 see abstract ---	1-7
A	DATABASE WPI Section Ch, Week 9136, Derwent Publications Ltd., London, GB; Class E16, AN 91-262356 & JP,A,3 170 583 (MATSUSHITA ELEC IND KK) 24 July 1991 see abstract --- -/--	1-7

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A,4 943 388 (SHANKLAND) 24 July 1990 see claims 1,2 see abstract; tables 3,4 ---	1-7
A	WO,A,92 01762 (DU PONT DE NEMOURS) 6 February 1992 see abstract; claim 1; table 5 -----	1-7

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

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